REMARKS

The above amendment to the claims has been made to incorporate the changes made under PCT Article 34 amendment, to correct the multiple dependency of the claims and to place the application in better condition for examination. An English translation of the PCT Article 34 amendment is also enclosed.

If any fees are due in connection with this paper, please charge our Deposit Account No. 50-2866.

Respectfully submitted,
WESTERMAN, HATTORI, DANIELS & ADRIAN, LLP

Stephen G. Adrian
Attorney for Applicants
Registration No. 32,878
Telephone: (202) 822-1100
Facsimile: (202) 822-1111

SGA/yap
Enclosures: English translation Art. 34 Amendment.

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English Translation of Amendment under PCT Article 34

PCT/JP2003/007554

portions is not etched largely.

When a metal oxide dissolving agent and a metal inhibitor are added as described above to annex chemical reaction effect, the polishing speed based on CMP is improved and further an effect that damage of the metal layer surface subjected to the CMP decreases is obtained.

Meanwhile, a conductor film made of tungsten, tungsten nitride, a tungsten alloy, a different tungsten compound, or the like is formed, as a barrier layer, beneath copper or a copper alloy of wiring in order to prevent copper from diffusing into an interlayer insulating film therebelow. It is therefore necessary to use CMP to remove the barrier layer exposed in any other portion than the wiring portion in which the copper or the copper alloy is buried. However, the conductor film for the barrier layer has a higher hardness than the copper or the copper alloy; therefore, according to any combination of polishing materials for the copper or the copper alloy, a sufficient CMP speed cannot be obtained. Accordingly, the following problem is caused: while the barrier layer is removed by CMP, the copper, the copper alloy or the like is etched; consequently, the wiring thickness lowers.

The present invention provides a polishing slurry for metal which makes its polishing speed sufficiently high while its etching speed is kept low, restrains corrosion and dishing of a metal surface, and makes it possible to form a metal-film-buried pattern having a high reliability.

The present invention also provides a metal polishing method which makes its polishing speed sufficiently high while its etching speed is kept low, restrains corrosion and dishing of a metal surface,

and makes it possible to form a metal-film-buried pattern having a high reliability with a good productivity, workability and yield.

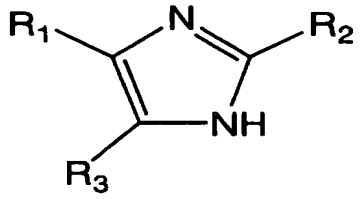
DISCLOSURE OF THE INVENTION

The polishing slurry of the present invention relates to a polishing slurry for metal and a polishing method according to the following (1) to (18):

(1) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring; and

a compound having an imidazole skeleton and represented by the following general formula (I):



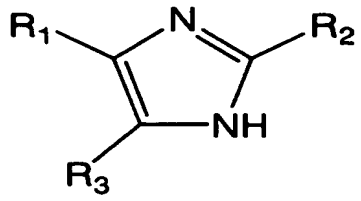
(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded.

(2) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having a triazole skeleton having no amino group; and

a compound having an imidazole skeleton and represented by the following general formula (I):



(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded.

(3) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring; and

a compound having a triazole skeleton having no amino group.

(4) The polishing slurry according to the above-mentioned (1) or (3), wherein the compound having the amino-triazole skeleton is 3-amino-1,2,4-triazole.

(5) The polishing slurry according to the above-mentioned (1) or (2), wherein the compound having the imidazole skeleton is at least one selected from the group consisting of 2-methylimidazole, 2-ethylimidazole, 2-(isopropyl)imidazole, 2-propylimidazole, 2-butylimidazole, 4-methylimidazole, 2,4-dimethylimidazole, and 2-ethyl-4-methylimidazole.

(6) The polishing slurry according to the above-mentioned (2) or (3), wherein the compound having the triazole skeleton having no amino group is at least one selected from the group consisting of 1,2,3-triazole, 1,2,4-triazole, benzotriazole, and 1-hydroxybenzotriazole.

(7) The polishing slurry according to any one of the

above-mentioned (1) to (6), wherein the metal inhibitor comprises the compound having the amino-triazole skeleton, the compound having the triazole skeleton having no amino group, and the compound having the imidazole skeleton.

(8) The polishing slurry for metal according to any one of the above-mentioned (1) to (7), further comprising a water-soluble polymer.

(9) The polishing slurry for metal according to the above-mentioned (8), wherein the water-soluble polymer is at least one selected from polysaccharides, polycarboxylic acids, polycarboxylic acid esters, polycarboxylic acid salts, polyacrylamide, and vinyl polymers.

(10) The polishing slurry for metal according to any one of the above-mentioned (1) to (9), wherein the oxidizer for metal is at least one selected from the group consisting of hydrogen peroxide, nitric acid, potassium periodate, hypochlorous acid, persulfates, and ozone water.

(11) The polishing slurry for metal according to any one of the above-mentioned (1) to (10), wherein the metal oxide dissolving agent is at least one selected from the group consisting of organic acids, organic acid esters, ammonium salts of organic acids, and sulfuric acid.

(12) The polishing slurry for metal according to any one of the above-mentioned (1) to (11), further comprising an abrasive.

(13) The polishing slurry for metal according to any one of the above-mentioned (1) to (12), wherein a metal film to be polished is at least one selected from the group consisting of copper, copper alloys, copper oxides, oxides of copper alloys,

tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

(14) A method for polishing a metal film by supplying the polishing slurry for metal according to any one of the above-mentioned (1) to (13) onto a polishing cloth of a polishing table while moving the polishing table and a substrate having the metal film relatively in the state that the substrate is pressed against the polishing cloth.

(15) The polishing method according to the above-mentioned (14), wherein the metal film is at least one selected from the group consisting of copper, copper alloys, copper oxides, oxides of copper alloys, tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

(16) The polishing method according to the above-mentioned (14) or (15), wherein a laminate of two or more metal films is continuously polished.

(17) The polishing method according to the above-mentioned (16), wherein a first film which is first polished among the two or more metal laminated films is one or more selected from copper, copper alloys, copper oxides, and oxides of copper alloys, and a second film which is next polished among them is one or more selected from tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

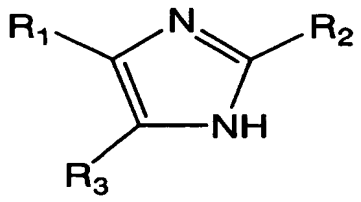
(18) A polishing method, comprising a first polishing step of polishing a wiring metal layer of a substrate, the substrate comprising an interlayer insulating film which has a surface consisting of concave portions and convex portions, a barrier layer which covers the interlayer insulating film along the surface

thereof, and a wiring metal layer which fills the concave portions to cover the barrier layer, and thereby making the barrier layer at the convex portions exposed, and a second polishing step of polishing at least the barrier layer and the wiring metal layer at the concave portions after the first polishing step, thereby making the interlayer insulating layer at the convex portions exposed, wherein the polishing is performed by use of the polishing slurry for metal according to any one of the above-mentioned (1) to (13) at least in the second polishing step.

BEST MODES FOR CARRYING OUT THE INVENTION

The present invention will be described in detail hereinafter.

The polishing slurry for metal of the invention comprises, as main constituent components, an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water. The metal inhibitor comprises a compound (A) having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring and a compound (B) having an imidazole skeleton and represented by the following general formula (I):



(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded; or comprises the compound (B) and a compound(C) having a triazole

skeleton having no amino group; or

comprises the compound (A) and the compound(C).

polishing method of the invention, but also a manner of bringing a brush made of metal or resin into contact with the surface to be polished and a manner of blowing a polishing slurry thereon at a given pressure.

At least in the second polishing step out of the first and second polishing steps, a polishing slurry of the present invention is used to perform polishing. A polishing slurry of the invention may be continuously used in the first and second polishing steps to perform polishing. In this case, it is particularly unnecessary to conduct the step of washing the face to be polished, the step of drying the face, or any other step between the first and second polishing steps. The process may be stopped therebetween in order to exchange polishing tables and polishing cloths, or change the working load or the like. The polishing slurries of the invention used in the first and second polishing steps may have the same composition or different compositions. In the case that the polishing slurries have the same composition, the polishing can be continued from the first polishing step to the second polishing step without stopping the process. Thus, this case is excellent in productivity.

An interlayer insulating film, a barrier layer and a wiring metal layer are further formed onto the thus-formed metal wiring. This is polished to make the whole of the semiconductor substrate smooth, thereby forming a second metal wiring layer. This process is repeated given times, thereby producing a semiconductor device having desired number of wiring layers.

EXAMPLES

The present invention will be described by way of the following examples. The invention is not limited by these examples.

[Examples 1 to 4, 6 to 11, Reference Examples 1 and 2 and Comparative Examples 1 and 2]

(Method for producing polishing slurries for metal)

Polishing slurries for metal were each prepared by mixing: 0.15% by weight of malic acid; 0.15% by weight of a water-soluble polymer (an acrylic polymer, weight-average molecular weight: about 10000); 0.2% by weight of an aminotriazole compound shown in Table 1 or 2; 0.2% by weight of a benzotriazole shown in Table 1 or 2 and/or 0.05% by weight of an imidazole compound shown therein as one or more metal inhibitors other than the aminotriazole compound; 9% by weight of hydrogen peroxide; and water as the balance; the ratio of each of these being a ratio thereof to the total amount.

The resultant polishing slurries for metal were each used to perform etching and CMP polishing under conditions described below and then make evaluation. Table 1 shows each polishing speed in the CMP for a copper substrate and each etching speed thereto together, and Table 2 shows each polishing speed for a tungsten substrate and each etching speed thereto together.

(Polishing conditions)

Copper substrate: a silicon substrate on which metal copper of 1500 nm thickness was deposited

Tungsten substrate: a silicon substrate on which a tungsten compound of 600 nm thickness was deposited

Polishing slurry supplying amount: 15 cc/minute

Polishing pad: foamed polyurethane resin (model number: IC1000, manufactured by Rodel)

Polishing pressure: 29.4 kPa (300 gf/cm^2)

Relative speed between the substrate and the polishing table: 45 m/minute, and polishing table rotating speed: 75 rpm

(Items for evaluation)

Polishing speed: the difference between the film thicknesses of each of the films before and after the polishing was obtained by the conversion of the electric resistance values thereof.

Etching speed: each of the substrates was immersed into each of the polishing slurries for metal which were stirred (room temperature, 25°C, stirring: 600 rpm), and the difference between the film thicknesses of each of the metal layers before and after the immersing was obtained by the conversion of the electric resistance values thereof.

[Examples 13 to 20, Reference Examples 3 to 6, and Comparative Example 3]

(Method for producing polishing slurries for metal)

Polishing slurries for metal were each prepared by mixing: 0.15% by weight of malic acid; 0.15% by weight of a water-soluble polymer (an acrylic polymer, weight-average molecular weight: about 10000); 0.2% by weight of an imidazole compound shown in Table 3; 0.2% by weight of a benzotriazole or 3-amino-1,2,4-triazole shown in Table 3; 9% by weight of hydrogen peroxide; and water as the balance; the ratio of each of these being a ratio thereof to the total amount.

The resultant polishing slurries for metal were each used to perform etching and CMP polishing and then make evaluation in

the same way as in Example 1. Table 3 shows each etching speed together.

(Table 1)

	Amino-triazole	Metal inhibitor	Copper (unit: nm/minute)	
			Polishing speed	Etching speed
Example 1	3-amino-1,2,4-triazole	benzotriazole	173.4	0.27
Example 2	3-amino-1,2,4-triazole	2-butyl imidazole benzotriazole	221.9	0.46
Example 3	3-amino-1,2,4-triazole	2-ethyl-4-methylimidazole benzotriazole	188.4	0.20
Example 4	3-amino-1,2,4-triazole	2,4-dimethyl imidazole benzotriazole	133.0	0.19
Reference Example 1	3-amino-1,2,4-triazole	None	132.2	2.50
Comparative Example 1	None	None	123.0	4.70

(Table 2)

	Amino-triazole	Metal inhibitor	Tungsten (unit: nm/minute)	
			Polishing speed	Etching speed
Example 6	3-amino-1,2,4-triazole	2-butyl imidazole	120.2	0.33
Example 7	3-amino-1,2,4-triazole	2-butyl imidazole benzotriazole	80.7	0.16
Example 8	3-amino-1,2,4-triazole	2-ethyl imidazole	116.0	1.21
Example 9	3-amino-1,2,4-triazole	2-(isopropyl) imidazole benzotriazole	163.0	1.24
Example 10	3-amino-1,2,4-triazole	2-propyl imidazole benzotriazole	147.0	1.51
Example 11	3-amino-1,2,4-triazole	2,4-dimethyl imidazole benzotriazole	81.0	0.37
Reference Example 2	3-amino-1,2,4-triazole	None	82.2	2.00
Comparative Example 2	None	None	30.2	2.53

(Table 3)

	Metal inhibitor	Etching speed (nm/minute)	
		Copper	Tungsten
Example 13	2-methyl imidazole benzotriazole	0.30	1.00
Example 14	2-ethyl imidazole benzotriazole	0.03	1.21
Example 15	2-(isopropyl) imidazole benzotriazole	0.19	1.24
Example 16	2-propyl imidazole benzotriazole	0.13	1.51
Example 17	2-butyl imidazole benzotriazole	0.46	0.16
Example 18	4-methyl imidazole benzotriazole	0.09	0.15
Example 19	2,4-dimethy limidazole benzotriazole	0.19	0.37
Example 20	2-ethyl-4-methyl imidazole benzotriazole	0.20	0.86
Reference Example 3	2-butyl imidazole	1.80	0.33
Reference Example 4	4-methyl imidazole	2.12	1.40
Reference Example 5	2,4-dimethyl imidazole	1.69	0.36
Reference Example 6	3-amino-1,2,4-triazole	2.50	2.00
Comparative Example 3	benzotriazole	2.50	10.00

In each of Examples 1 to 4, Reference Example 1, the speed of polishing copper was 130 nm/minute or more, and was better than in Comparative Example 1. The etching speed was also a sufficiently lower than in the Comparative Example.

In each of Examples 6 to11, Reference Example 2, the speed of polishing tungsten was 80 nm/minute or more, and was better than in Comparative Example 2. The etching speed was also a sufficiently lower than in the Comparative Example.

In each of Examples 13 to 20, the speed of etching copper was 0.5 nm/minute or less, and was much better than in Comparative Example 3. About tungsten also, the etching speed was a sufficiently lower than in the Comparative Example. In each of Reference Examples 3 to 6, the etching speed was sufficiently lower about tungsten, and was at a practical level.

In each of Examples 13 to 20, Reference Examples 3 to 6, the speed of polishing copper and that of polishing tungsten were 100 nm/minute or more and 20 nm/minute or more, respectively, and were at a sufficiently practical level.

[Example 25]

A polishing slurry for metal was prepared by mixing: 0.15% by weight of malic acid; 0.15% by weight of a water-soluble polymer (an acrylic polymer, weight-average molecular weight: about 10000); 0.3% by weight of 3-amino-1,2,4-triazole; 0.14% by weight of benzotriazole; 0.05% by weight of 2,4-dimethylimidazole; 0.4% by weight of an abrasive (colloidal silica, primary particle diameter: 30 nm); 9% by weight of hydrogen peroxide; and water as the balance.

Trenches of 0.5 to 100 μm depth were made in silicon dioxide, and a tungsten layer of 50 nm thickness was formed as a barrier layer by a known method. A copper film was formed thereon so as to have a thickness of 1.0 μm. A silicon substrate was thus prepared. The substrate was polished with the above-mentioned polishing slurry under the same conditions as in Example 1 until convex portions of the silicon dioxide were exposed in the entire surface of the substrate. The time for the polishing was 2 minutes, and a polishing speed of about 500 nm/minute or more was obtained.

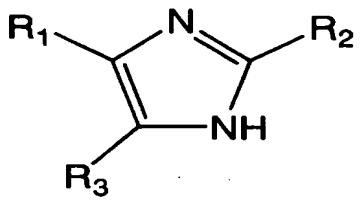
Next, a tracer type level meter was used to obtain the decreased amount of the film thickness of the wiring metal regions with respect to that of the insulating film regions, from the surface shape of a stripe-form pattern wherein wiring metal regions 100 μm in width and insulating film regions 100 μm in width were alternately arranged. As a result, the amount was 70 nm, and was a sufficiently practical value.

CLAIMS

1. (Amended) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring; and

a compound having an imidazole skeleton and represented by the following general formula (I):



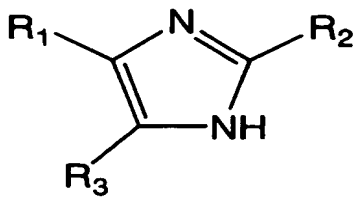
(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded.

2. (Amended) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having a triazole skeleton having no amino group; and

a compound having an imidazole skeleton and represented by the following general formula (I):



(I)

wherein R_1, R_2 and R_3 each independently represent a hydrogen atom, an amino group, or a C_1-C_{12} alkyl chain provided that the case that all of R_1, R_2 and R_3 are hydrogen atoms is excluded.

3. (Amended) A polishing slurry for metal, comprising an oxidizer, a metal oxide dissolving agent, a metal inhibitor, and water, wherein the metal inhibitor comprises:

a compound having an amino-triazole skeleton wherein an amino group is bonded to carbon in a triazole ring; and

a compound having a triazole skeleton having no amino group.

4. (Amended) The polishing slurry according to claim 1 or 3, wherein the compound having the amino-triazole skeleton is 3-amino-1,2,4-triazole.

5. (Amended) The polishing slurry according to claim 1 or 2, wherein the compound having the imidazole skeleton is at least one selected from the group consisting of 2-methylimidazole, 2-ethylimidazole, 2-(isopropyl)imidazole, 2-propylimidazole, 2-butylimidazole, 4-methylimidazole, 2,4-dimethylimidazole, and 2-ethyl-4-methylimidazole.

6. (Amended) The polishing slurry according to claim 2 or 3, wherein the compound having the triazole skeleton having no amino group is at least one selected from the group consisting

of 1,2,3-triazole, 1,2,4-triazole, benzotriazole, and 1-hydroxybenzotriazole.

7. (Amended) The polishing slurry according to any one of claims 1 to 6, wherein the metal inhibitor comprises the compound having the amino-triazole skeleton, the compound having the triazole skeleton having no amino group, and the compound having the imidazole skeleton.

8. (Amended) The polishing slurry for metal according to any one of claims 1 to 7, further comprising a water-soluble polymer.

9. (Amended) The polishing slurry for metal according to claim 8, wherein the water-soluble polymer is at least one selected from polysaccharides, polycarboxylic acids, polycarboxylic acid esters, polycarboxylic acid salts, polyacrylamide, and vinyl polymers.

10. (Amended) The polishing slurry for metal according to any one of claims 1 to 9, wherein the oxidizer for metal is at least one selected from the group consisting of hydrogen peroxide, nitric acid, potassium periodate, hypochlorous acid, persulfates, and ozone water.

11. (Amended) The polishing slurry for metal according to any one of claims 1 to 10, wherein the metal oxide dissolving agent is at least one selected from the group consisting of organic acids, organic acid esters, ammonium salts of organic acids, and sulfuric

acid.

12. (Amended) The polishing slurry for metal according to any one of claims 1 to 11, further comprising an abrasive.

13. (Amended) The polishing slurry for metal according to any one of claims 1 to 12, wherein a metal film to be polished is at least one selected from the group consisting of copper, copper alloys, copper oxides, oxides of copper alloys, tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

14. (Amended) A method for polishing a metal film by supplying the polishing slurry for metal according to any one of claims 1 to 13 onto a polishing cloth of a polishing table while moving the polishing table and a substrate having the metal film relatively in the state that the substrate is pressed against the polishing cloth.

15. (Amended) The polishing method according to claim 14, wherein the metal film is at least one selected from the group consisting of copper, copper alloys, copper oxides, oxides of copper alloys, tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

16. (Amended) The polishing method according to claim 14 or 15, wherein a laminate of two or more metal films is continuously polished.

17. (Amended) The polishing method according to claim 16, wherein a first film which is first polished among the two or more metal laminated films is one or more selected from copper, copper alloys, copper oxides, and oxides of copper alloys, and a second film which is next polished among them is one or more selected from tantalum and compounds thereof, titanium and compounds thereof, and tungsten and compounds thereof.

18. (Amended) A polishing method, comprising a first polishing step of polishing a wiring metal layer of a substrate, the substrate comprising an interlayer insulating film which has a surface consisting of concave portions and convex portions, a barrier layer which covers the interlayer insulating film along the surface thereof, and a wiring metal layer which fills the concave portions to cover the barrier layer, and thereby making the barrier layer at the convex portions exposed, and a second polishing step of polishing at least the barrier layer and the wiring metal layer at the concave portions after the first polishing step, thereby making the interlayer insulating layer at the convex portions exposed, wherein the polishing is performed by use of the polishing slurry for metal according to any one of claims 1 to 13 at least in the second polishing step.

19. (Canceled)

20. (Canceled)